SOIL FERTILITY

Soil Properties and Clover Establishment Six Years after Surface Application of Calcium-Rich By-Products

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ABSTRACT

Calcium-rich soil amendments can improve plant growth by supplying Ca and reducing detrimental effects of soil acidity, but solubility and neutralizing capacity of Ca sources vary. Our objectives were to evaluate effects of calcitic dolomite and several coal combustion by-products on soil properties at various depths 6 yr after surface application and their influence on grass-clover herbage accumulation. Calcium and Mg soil amendments were surface-applied to an acidic grassland in 1993, and orchardgrass (Dactylis glomerata L.) and tall fescue [Lolium arundinaceum (Schreb.) Darbyshire] were oversown in 1994. In 1998, amendment treatment plots were split to accommodate sod seeding with red clover (Trifolium pratense L.) or white clover (T. repens L.) as well as a nonseeded control. No N fertilizer was applied after sod seeding. Six years after amendment application, reductions in soil Al and Mn and increases in Ca and pH from 4654 kg ha⁻¹ calcitic dolomite, 15 000 kg ha⁻¹ fluidized bed combustion residue, or 526 kg ha⁻¹ MgO amendment were greatest in the surface 2.5 cm while rates of gypsum as high as 32 000 kg ha⁻¹ left little residual effect except for decreases in Mg. Percentage clover in the sward tripled as pH increased from 4.3 to 5.0 while herbage mass increased 75% as clover percentage increased. Herbage mass was generally more closely correlated with properties of soil samples collected from the surface 2.5 cm than from deeper samples.

Because of Limitations imposed by steep or rocky terrain, renovation of low-fertility pasture soils in Appalachia often is accomplished with surface application of liming amendments and nutrients rather than incorporation. Surface application is less expensive and reduces erosion caused by exposure of tilled soil to heavy rains before plant cover is achieved. Limestone, the most commonly used amendment, supplies Ca and Mg, and the carbonate component raises soil pH and reduces levels of soil Al³+, Mn²+, and H+. However, beneficial effects of surface-applied limestone move downward slowly unless large amounts are added (Brown et al., 1956). Toxic levels of Mn and Al in layers beneath the amended soil may restrict rooting or nodulation of acid-sensitive plants such as clovers.

Gypsum (CaSO₄·2H₂O) is a more soluble amendment that quickly increases soil solution Ca concentration and thus reduces the proportion of Al to total cations, thereby reducing toxicity. Although gypsum does not chemically neutralize Al or raise pH the way that limestone does (and therefore has a calcium carbonate equivalency of zero), the sulfate component of gypsum

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Published in Agron. J. 96:1531–1539 (2004). © American Society of Agronomy 677 S. Segoe Rd., Madison, WI 53711 USA can react with oxides of Fe and Al present in certain highly weathered soils to release OH⁻ ions and raise pH slightly (Rajan, 1978). A number of gypsum-containing by-products of scrubbing SO₂ from emissions of coal-fired power plants are available, and various experiments in the northeastern and southeastern United States demonstrate their utility in improving productivity (Sumner et al., 1986; Shainberg et al., 1989; Stout and Priddy, 1996). In Georgia, maize (*Zea mays* L.) yield improvements were observed 16 yr after gypsum application to a Typic Kandhapludult soil (Toma et al., 1999). Information on longevity of beneficial effects of by-product gypsum on soils typical of the northeastern USA is lacking.

The purpose of this experiment was to evaluate residual effects of surface-applied Ca-rich materials on soil properties of an abandoned acidic Appalachian grassland and measure productivity of acid-sensitive forage species. Specifically, the objectives were to (i) compare duration and extent of effects of gypsum with those of calcitic dolomite; (ii) determine the amount of Mg left in the soil where MgO, calcitic dolomite, and Mg-enriched gypsum were applied; (iii) determine the effect of soil acidity on clover establishment and herbage yield; and (iv) determine sampling depth effects on correlation of soil test results with herbage yields.

MATERIALS AND METHODS

The experiment was part of a larger investigation in which red and white clover were sod-seeded into an existing tall fescue-orchardgrass grassland experiment to examine effects of soil properties on clover establishment and herbage yield. The tall fescue-orchardgrass experiment was installed in an area that had been cleared after three decades of abandonment, then rotary-mowed for 10 yr without addition of fertilizer or amendment. As described by Ritchey and Snuffer (2002), this acidic grassland received 12 surface amendment and fertilizer treatments applied in 1993 in a randomized complete block design using varying levels of calcitic dolomite, MgO, and three coal combustion by-products (Tables 1 and 2) and was then overseeded with orchardgrass and tall fescue. After amendment, the area was harvested for herbage for 4 yr. In addition to the 10 treatments discussed by Ritchey and Snuffer (2002), we evaluated yields from two treatments of fluidized bed combustion residue (FBC) also applied in 1993 that they did not discuss. This material, an alkaline bed ash by-product resulting from injection of limestone with coal into the boiler, was surface-applied at 7500 kg ha⁻¹ (treatment $F_{75}MgO$) and 15 000 kg ha⁻¹ (treatment $F_{15}MgO$) (Table 2). Because of its content of CaO, Ca(OH)₂, and CaCO₃, FBC can be used as a liming agent (Stehouwer et al., 1999), but its

Abbreviations: FBC, fluidized bed combustion residue; LSD, least significant difference; TCE, total calcium carbonate equivalent.

Table 1. Chemical and physical properties (Ca, Mg, and S concentration; calcium carbonate equivalent; and particle size distribution) of amendments surface-applied to a Typic Hapludults infertile abandoned grassland soil in southern West Virginia.

		Elemo	ental concen	tration	Particle size distribution					
Amendment	Ca Mg		s	Calcium carbonate equivalent	<0.125 mm	0.125 to 0.250 mm	>0.250 mm			
		— g kg ⁻¹ —			g 100 g ⁻¹	— g 100 g ⁻¹ —				
Calcitic dolomite	210	110	0	104	17	37	46			
MgO amendment	0	510	0	245	†					
By-product gypsum no. 22‡ Fluidized bed combustion	238	0.23	216	5	25	46	29			
residue no. 26‡ Mg-enhanced by-product	414	3.65	174	55	†					
gypsum no. 27‡	209	23	177	13	74	22	4			

[†] Particle size range for MgO fertilizer (1 to 2.8 mm) is designed to allow blending with granulated fertilizers. Fluidized bed combustion residue is also a granular material.

Mg content is low (Table 1), so the FBC treatments also received 526 kg ha⁻¹ MgO (Table 2).

The soil at the site near Bragg, WV (37°48′45″ N, 80°58′ 45″ W), was mapped as a Gilpin silt loam (fine-loamy, mixed, mesic, Typic Hapludult). Less than 2 wk after receiving 10 cm of precipitation, the plots (8 by 3 m) from the original experiment were split into three subplots of 2.7 by 3 m and sod-seeded 31 Mar. 1998 with a Tye¹ seeder (Tye Co., Lockney, TX) with (i) 'Cinnamon' red clover (9.2 kg ha⁻¹) or (ii) 'Huia' white clover (4.4 kg ha⁻¹) or (iii) left unseeded. No effort was made to suppress grass vegetation. A different randomization of subplots was used for each of the four replications.

Annual broadcast fertilizer applications 2 Apr. 1998 and 2 Apr. 1999 consisted of 112 kg ha⁻¹ P and 213 kg ha⁻¹ K applied as 0–25–25. Previous broadcast fertilizer applications (1993 to 1997) totaled 628 kg ha⁻¹ N, 244 kg ha⁻¹ P, and 448 kg ha⁻¹ K (Ritchey and Snuffer, 2002).

We evaluated herbage accumulation by using a rotary

mower equipped with herbage collection system to clip an area 0.66 by 2.43 m in the center of the subplots to a 5-cm height on 22 June, 7 Aug., and 5 Oct. in 1998 and 28 May and 20 Sept. in 1999. Herbage on the rest of the subplot was cut and removed. Herbage dry matter content was determined on grab samples that were oven-dried for 36 h at 67°C. A point-quadrat method with 10-cm intervals in a 0.16- or 0.25-m² area (to provide 16 or 25 evaluation points per subplot) was used to determine botanical composition on 21 Apr., 18 June, and 30 Sept. in 1998 and 5 May in 1999.

Soil samples from 0- to 2.5-, 2.5- to 5-, 5- to 10-, and 10- to 15-cm depths were collected 3 to 10 Aug. 1999 (nine subsamples per plot). Soil analyses consisted of inductively coupled plasma emission spectroscopy measurement of neutral 1 M NH₄OAc-extractable Ca, Mg, K, S, and Mn (Thomas, 1982) and KCl-extractable Al (Barnhisel and Bertsch, 1982). Soil pH (1:1 w/w soil/water) was measured with a Sentron field effect transistor electrode (Sentron Integrated Sensor Technol., Federal Way, WA). Organic C measurements were made on samples from each depth of each replication of treatments G_0 and G_0L , using a mass spectrometer equipped with an elemental analyzer.

Table 2. Production of herbage harvested in 1999 from subtreatments sod-seeded to red or white clover on coal combustion by-product (CCBP) treatments surface-applied in 1993 to an acidic Appalachian grassland. The first five treatments provide a gypsum response profile under limed conditions, the following two examine the use of a fluidized bed combustion product as a limestone substitute, and the remaining show contrasts without calcitic dolomite. Amount of MgO amendment added and total amounts of Mg, S, and Ca added as amendments are given.

	Amount	Amount	T	otal amount ad	ded	Amendment	1999 Grass-clover herbage yield	
Treatment	CCBP	MgO	Mg	S	Ca	TCE†	White	Red
				kş	g ha ⁻¹ ————			
		T	reatments with	4654 kg ha ⁻¹ ca				
G_0L	0	0	512	0	977	4840	2035	1776
G_1L	1 000‡	0	512	216	1215	4890	1906	1642
$\dot{G_8L}$	8 000‡	0	514	1728	2881	5240	1885	1784
$G_{16}L$	16 000‡	0	516	3456	4793	5640	1994	1903
$G_{32}L$	32 000‡	0	519	6912	8609	6440	1711	2043
			Treatments	without calcitic	dolomite			
F _{7.5} MgO	7 500§	526	295	1279	3095	5419	1930	1754
F ₁₅ MgO	15 000§	526	322	2558	6190	9548	1921	1915
\mathbf{G}_{0}	0	0	0	0	0	0	1326	1111
G ₀ MgO	0	526	268	0	0	1290	1447	1317
G_8	8 000‡	0	0	1728	1904	400	1172	990
G ₈ MgH	8 400¶	0	0	1492	1772	1110	1088	1269
G ₁₆ MgO	16 000‡	526	268	3456	3808	2090	1513	1643
	d LSD (0.05)						606	622

[†] TCE = total CaCO $_3$ equivalency. All of the amendments had some potential to neutralize soil acidity. The CaCO $_3$ equivalency values ranged from 5% for by-product gypsum up to 245% for MgO fertilizer (Table 1). We calculated the TCE per treatment by summing the neutralizing capabilities of each amendment component as calculated by multiplying the CaCO $_3$ equivalency of the component by the quantity of that component included in the treatment. \ddagger G = wallboard-quality agricultural gypsum produced by a limestone-based, in-situ oxidation, wet scrubber desulfurization system (no. 22 in Table 1). \$ F = fluidized bed combustion by-product (no. 26 in Table 1).

[‡] This and additional information about by-products no. 22, 26, and 27 are given in Clark et al. (1995).

¹The mention of trade or manufacturer names is made for information only and does not imply an endorsement, recommendation, or exclusion by USDA-ARS.

[¶] MgH = experimental Mg-enhanced gypsum product containing 23 g kg⁻¹ Mg as Mg(OH)₂ (College et al., 1997) (no. 27 in Table 1).

Calcium carbonate equivalency of amendments was determined using a boiling HCl (0.05 M) digestion and back-titrating with NaOH (0.05 M) to the phenolphthalein end point. Total calcium carbonate equivalent (TCE) for the treatments was calculated by summing the individual calcium carbonate equivalents for each component. Calcium saturation and Al saturation were calculated as extractable Ca or Al divided by the sum of extractable Al, Ca, Mg, K, and Mn. To estimate what potential values for soil parameters would have been if we had composited by depth the samples making up the 0- to 5-, 0- to 10-, and 0- to 15-cm layers, we used weighted means of parameters measured in each individual layer, i.e., values were corrected for depth of each individual layer and for bulk density of soil in that layer. Bulk density values were 1.07, 1.22, 1.40, and 1.49 Mg m⁻³ for the 0- to 2.5-, 2.5- to 5-, 5- to 10-, and 10- to 15-cm depths.

Analysis of variance, Pearson correlation, and multiple regression evaluations were conducted using General Linear Model statistical procedures (SAS Inst., 1990). Yearly herbage yields were calculated by summing individual cuttings. Data from several subplots were compromised because of stimulation of pasture growth by fungal fairy rings and because of excavations by woodchucks (*Marmota monax*); these data were treated as missing. When the analysis-of-variance *F* test was significant at the 0.05 probability level, least significant differences were calculated to test differences among means. All differences and regressions discussed were significant at the 0.05 probability level unless otherwise stated.

RESULTS AND DISCUSSION

Soil Characteristics in Treatment not Receiving Amendments

The control treatment (G_0) received the same NPK fertilizers as the other treatments but no amendments. Control treatment levels of organic C, Ca, Mg, and Mn were greater in the surface 2.5 cm than in the lower horizons (Fig. 1), but pH, which averaged 4.31, did not vary significantly with depth. Levels of Ca, Mg, K, and Mn were highly correlated with organic C $(r^2$ of 0.984,

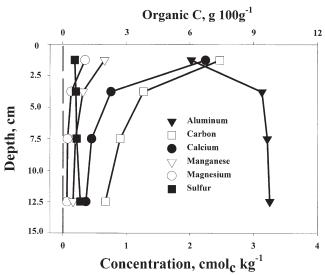


Fig. 1. Concentrations of extractable cations (bottom axis) and soil C (top axis) at several depths in treatment G_0 where NPK fertilizers but no liming amendments were added. The soil is a Gilpin silt loam (Typic Hapludults) in a grassland in southern West Virginia that had been abandoned for 40 yr before initiation of the experiment.

0.987, 0.996, and 0.997, respectively). Disproportionately greater concentrations of cations and organic C in surface layers have also been reported in other uncultivated soils. Jenkins (2002) found higher surface cation concentrations in four West Virginia forest soils and a high correlation between Ca and organic C. This is not unexpected as organic matter is a major contributor to cation exchange capacity, the ability of soil to hold cations against leaching (Brady, 1990). At low pH levels, organic matter can bind Al so strongly that it becomes difficult to extract chemically (Brady, 1990), and this may explain why measured levels of extractable Al were somewhat lower in the 0- to 2.5-cm layer where organic matter concentration was highest.

To evaluate element contents in the entire surface 15 cm of soil, we summed the amounts present in each layer as calculated using mean bulk density and thickness for that layer. The quantities of extractable elements in the surface 15 cm of the unamended control treatment that received only fertilizer were (in kg ha⁻¹) 284, 29, 558, 75, and 146 for Ca, Mg, Al, S, and Mn, respectively.

Soil Characteristics in Treatments Receiving Amendments

Calcium

Net changes in levels of exchangeable Ca due to surface application of amendments were calculated by comparison with levels in the unamended control (G_0) and varied with the associated anion (Fig. 2). Amendments with high TCE values increased concentrations more than amendments with low TCE. For high TCE amendments, effects tended to be concentrated in the surface 0- to 2.5-cm layer. For example, in treatment G_0L , where Ca was added as calcitic dolomite [CaMg(CO₃)₂ plus a small amount of CaCO₃], the increase in concentration

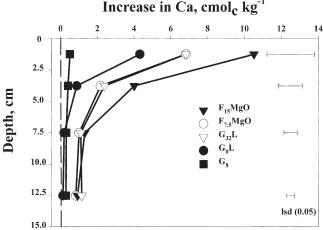


Fig. 2. Increase in Ca at various depths sampled 6 yr after surface application of amendments to a Typic Hapludults abandoned grassland in southern West Virginia for selected treatments: (i) 15 000 kg ha $^{-1}$ fluidized bed combustion residue (FBC) + 526 kg ha $^{-1}$ MgO (F_{15} MgO), (ii) 7500 kg ha $^{-1}$ FBC + 526 kg ha $^{-1}$ MgO ($F_{7.5}$ MgO), (iii) 32 000 kg ha $^{-1}$ gypsum + 4654 kg ha $^{-1}$ calcitic dolomite (G_{02} L), (iv) 4654 kg ha $^{-1}$ calcitic dolomite (G_{0} L), and (v) 8000 kg ha $^{-1}$ gypsum (G_{8}). Increases were calculated by comparing measured values with those found in the unamended treatment that received only fertilizer (G_{0}).

of Ca detected in the surface layer was 37 times greater than the increase in the 10- to 15-cm layer. In treatment G_8 , where Ca had been added as sulfate, the increase in Ca concentration at 0 to 2.5 cm was less than two times greater than that in the 10- to 15-cm layer.

The Ca distribution in the limed and fertilized treatment (G₀L) was close to the distribution reported by Bryan and Elliott (1991) 4 yr after uncultivated Westmoreland and Clarksburg (Aquic and Ultic Hapludalf, respectively) soils were surface-treated with 4500 kg ha⁻¹ limestone. However, in long-term no-till pastures on loess-derived soils, changes with depth for Ca were much more gradual, perhaps due to higher Ca levels in the parent material (Rhoton, 2000). Similarly, a Georgia pasture established for 15 yr also had more gradual nutrient concentration gradients with soil depth, even with redeposition of nutrients by animals on the soil surface (Schomberg et al., 2000). Perhaps a stronger effect was lacking because previous incorporations increased nutrient levels at greater depths, in contrast to our site where no nutrients or amendments were added for 40 vr.

To calculate the increase in amounts of Ca present in the surface 15 cm of the profile attributable to amendments, we subtracted the levels present in the fertilizer-only control treatment (G_0) to obtain the change and then compared the increase to the total amount of Ca added as amendment (Table 3). In treatment G_0L (the calcitic dolomite treatment), 34% of the 980 kg ha⁻¹ Ca added was extractable from the top 15 cm while in the gypsum treatment (G_8), only 7% of the 1900 kg ha⁻¹ Ca added was extractable (Table 3).

Total amounts of exchangeable Ca found in the 0-to 15-cm layer were correlated with the total calcium carbonate equivalent of the amendments applied [Ca (kg ha⁻¹) = 309 + 0.111 TCE, r^2 = 0.83, P < 0.0001, n = 12], but the inclusion of the quantity of S added (a

measure of gypsum amendment application) did not significantly improve the correlation, underlining the small effect that even heavy gypsum additions had on Ca status 6 yr after application. Some of the differences in retention of Ca between gypsum and calcitic dolomite may be explained by reactions with soil minerals. As CaMg(CO₃)₂ particles react with adjacent soil, HCO₃ and CO₃²⁻ neutralization of exchangeable acidity frees exchange sites previously occupied by Al3+ and H+, providing new exchange sites for retention of Ca²⁺ and Mg²⁺ (Shamshuddin and Ismail, 1995). Cations thus have a place to stay in the soil while at the same time, there is no supply of soluble stable anions available for downward movement of Ca²⁺ or Mg²⁺ because at the pH of the soil solution, most of the CO₃²⁻ or HCO₃⁻ decomposes into CO2 gas. A cation cannot move downwards in the soil by itself (due to conservation of charge), so reduction of acidity in lower soil layers from surface application of calcitic dolomite is slow. On the other hand, sulfate anions do not react with most of the clay minerals in Gilpin soil (He et al., 1996), and few exchange sites for retention of Ca²⁺ are created. Moreover, gypsum is more than seven times more soluble than dolomite (Weast, 1978), and it forms a stable uncharged ion pair (Pavan et al., 1982), so it is relatively easy for it to be leached lower into the profile (He et al., 1996; Shamshuddin and Ismail, 1995).

Since only 34% of the Ca added as calcitic dolomite in treatment G_0L was extracted from the surface 15 cm (Table 3), what happened to the rest? Some of it may still have not dissolved, or it may have been solubilized by reactions with acid rain or N fertilizer and leached below 15 cm with sulfate or nitrate ions, lost by erosion, taken up by plants, moved downwards by soil fauna such as earthworms, or transformed into nonexchangeable forms.

Table 3. Change in 0- to 15-cm soil properties (compared with control treatment, G_0) and extractable residual calculated as percentage of added nutrients for 11 treatments applied to an abandoned grassland on an Typic Haplustult near Bragg, WV, sampled 6 yr after treatment application.

						Treatmen	ıt					
Observation	G_0L	G ₁ L	G ₈ L	$G_{16}L$	G ₃₂ L	G ₀ MgO	G_8	G ₈ MgH	G ₁₆ MgO	F _{7.5} MgO	F ₁₅ MgO	LSD 0.05
Ca												
change, kg ha ⁻¹	328	405	353	832	831	124	135	227	354	757	1149	359***
amount added, kg ha ⁻¹	977	1215	2881	4793	8609	0	1904	1772	3808	3095	6190	
residual, %	33.5	33.3	12.2	17.4	9.6	_	7.1	12.8	9.3	24.5	18.6	
pH												
increase in pH	0.31	0.39	0.23	0.47	0.40	0.19	0.02	0.09	0.20	0.47	0.73	0.20***
TCE^{\dagger} added, 1000 kg ha ⁻¹	4.84	4.89	5.24	5.64	6.44	1.291	0.4	1.11	2.09	5.42	9.55	
increase/TCE	0.064	0.08	0.045	0.083	0.060	0.146	0.478	0.081	0.096	0.087	0.077	
Al												
decrease in Al, kmolcha-1	-10.9	-8.96	-4.71	-21.5	-20.6	-10.1	-2.47	-7.11	-16.7	-12.0	-23.4	14.4‡
TCE added, kmolcha-1	96.8	97.8	104.8	112.8	128.8	25.8	8.0	22.2	41.8	108.5	191.0	
decrease/TCE, %	11.2	9.2	4.5	19	16	40	31	32	40	11.1	12.2	
Mg												
change, kg ha ⁻¹	89.4	99.5	43.2	61.3	20.1	96.8	-8.5	-1.0	55.2	35.2	1.7	31.3***
added, kg ha ⁻¹	512	512	514	516	519	268	0	187	274	295	322	
residual, %	17.5	19.4	8.4	11.9	3.9	36.1	_	-0.5	20.1	11.9	0.5	
S												
change, kg ha ⁻¹	-10.2	-9.0	9.9	14.5	64.4	-3.2	36.2	22.5	21.7	22.1	23.1	32.0**
added, kg ha ⁻¹	0	216	1728	3456	6912	0	1728	1492	3456	1279	2558	
residual, %	-	-4.2	0.6	0.4	0.9	-	2.1	1.5	0.6	1.7	0.9	

^{**}F test significant at the 0.01 probability level.

^{***} F test significant at the 0.001 probability level.

[†] TCE, total calcium carbonate equivalent.

 $[\]ddagger F$ test significant at the 0.07 probability level.

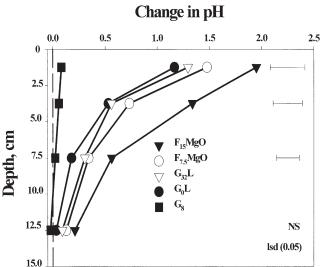


Fig. 3. Change in pH at various depths for selected treatments sampled 6 yr after surface application of amendments to a Typic Hapludults abandoned grassland in southern West Virginia. (Treatments are described in Fig. 2.) Changes were calculated by comparing measured values with those found in the unamended treatment that received only fertilizer (G_0).

pН

The pattern of pH changes with depth was generally similar to that of Ca with larger increases occurring near the surface (Fig. 3).

Because TCE is a measure of amendment ability to raise pH and neutralize acidity, soil pH and amendment TCE should be closely correlated. In our experiment, the relation between pH and TCE for the 0- to 15-cm layer as a whole was linear [pH = 4.33 + 0.0000697 TCE (kg ha⁻¹), $r^2 = 0.90$, P < 0.0001, n = 12]. For each 1000 kg ha⁻¹ TCE added 6 yr before, the pH in the 0- to 15-cm layer increased 0.07 units. This is close to the value of 0.08 unit pH change per 1000 kg of limestone applied per hectare for a similar range of TCE additions in a Gilpin soil in Pennsylvania, as calculated from data given by Lathwell and Reid (1984).

Gypsum had little residual effect on soil pH, as illustrated by treatment G₈ where no calcitic dolomite was added (Fig. 3; Table 3). This contrasts with results on more highly weathered soils containing higher contents of Fe and Al oxides where beneficial effects persisted for 10 or more years (Ritchey et al., 2000).

Aluminum

Extractable Al concentration was $2.0 \text{ cmol}_c \text{ kg}^{-1}$ in the surface 0- to 2.5-cm layer of the unamended treatment and about $3.2 \text{ cmol}_c \text{ kg}^{-1}$ in the three lower layers (Fig. 1). Application of amendments with 4840 kg ha⁻¹ or more TCE raised pH enough to neutralize almost all the extractable Al in the 0- to 2.5-cm layer (Fig. 4). The high FBC treatment (treatment $F_{15}\text{MgO}$) neutralized almost all the Al in the 0- to 2.5- and 2.5- to 5-cm layers. The efficiency of FBC in reducing Al in the second layer may be related to its $\text{Ca}(\text{OH})_2$ content, which is at least five times more soluble than dolomite (Weast, 1978). Or, the pH in the surface layer (6.3) may have been

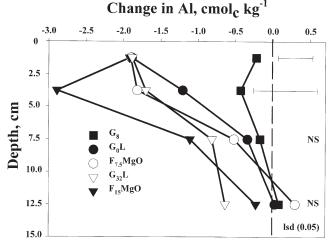


Fig. 4. Change in Al at various depths for selected treatments sampled 6 yr after surface application of amendments to a Typic Hapludults abandoned grassland in southern West Virginia. (Treatments are described in Fig. 2.) Changes were calculated by comparing measured values with those found in the unamended treatment that received only fertilizer (G_0) .

high enough to maintain stability of Ca(HCO₃)₂ in soil solution so that alkalinity from the FBC could leach into the 2.5- to 5.0-cm layer.

The effects of amendments on Al were less evident at greater depths, and at the 10- to 15-cm layer, the correlation between TCE of amendments and Al was not significant.

For the profile as a whole, the effects of amendments on reducing levels of extractable Al can be described by two relationships (Fig. 5), one for amendments with TCE of 2090 kg ha⁻¹ or less [Al (kmol_c ha⁻¹) = 62 – 0.401 TCE (kmol_c ha⁻¹), $r^2 = 0.99$, P = 0.0006, n = 5] and one for amendments with TCE of 4840 kg ha⁻¹ or higher where the response relationship for high TCE amendments (calcitic dolomite and FBC), including the

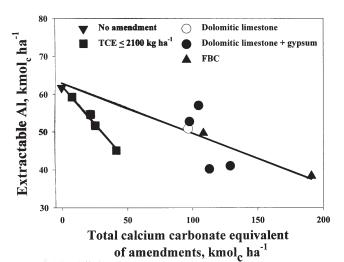


Fig. 5. Extractable Al in the surface 15 cm of a Typic Hapludults abandoned grassland in southern West Virginia as a function of total calcium carbonate equivalent (TCE) of amendments surface-applied in 1993. The relationship between Al and TCE for TCE values less than 2100 kg ha⁻¹ has a steeper slope than for higher TCE values. FBC, fluidized bed combustion residue.

zero treatment, was Al (kmol_c ha⁻¹) = 63 – 0.133 TCE (kmol_c ha⁻¹), r^2 = 0.68, P = 0.01, n = 8. The low TCE amendments decreased extractable Al by 0.40 kmol_c ha⁻¹ for each 1 kmol_c ha⁻¹ added. The higher TCE amendments decreased Al only 0.13 kmol_c ha⁻¹ for each 1 kmol_c ha⁻¹ of TCE added. The lower efficiency (Al neutralized per unit TCE) for high TCE treatments was partly because some neutralization potential was expended in raising pH after all Al was neutralized in the 0- to 2.5-cm layer. In addition, larger particle size (Table 2) may have limited dissolution of some of the calcitic dolomite and FBC.

Magnesium

Changes in Mg associated with amendments (Fig. 6) tended to be more marked in the 0- to 2.5-cm layer than in lower layers, as was the case for Ca (Fig. 2). Application of some amendments with high amounts of gypsum decreased Mg levels.

The amount of Mg present in the surface 5 cm in the control treatment (G_0) was 0.23 cmol_c kg⁻¹, which is less than the amount (0.41 cmol_c kg⁻¹) considered yield limiting (van Eck, 1990). The addition of calcitic dolomite or MgO fertilizer 6 yr earlier was sufficient to maintain an adequate Mg level, except in treatment F_{15} MgO. The addition of gypsum in the absence of a Mg supply (Treatment G_8) reduced soil Mg level to 0.18 cmol_c kg⁻¹ in the surface 5 cm of the profile.

The amount of Mg present in the total 15-cm depth was positively related to the amount of Mg added and negatively related to the amount of gypsum added (as estimated by total S in the amendments): Mg (kg ha⁻¹) = 9.55 + 0.159 Mg added (kg ha⁻¹) - 0.011 S added (kg ha⁻¹), $R^2 = 0.64$, P = 0.01, n = 12. Gypsum in the amendment decreased the amount of Mg present in the total 0- to 15-cm layer by about 11 kg ha⁻¹ per 1000 kg ha⁻¹ S added. Presumably, sulfate in the gypsum reacted with Mg to form MgSO₄ (Bohn et al., 1979), and this neutral ion pair leached through the profile.

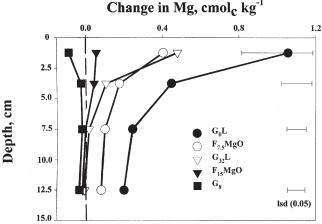


Fig. 6. Change in Mg at various depths for selected treatments sampled 6 yr after surface application of amendments to a Typic Hapludults abandoned grassland in southern West Virginia. (Treatments are described in Fig. 2.) Changes were calculated by comparing measured values with those found in the unamended treatment that received only fertilizer (G₀).

The amendment most effective in maintaining exchangeable Mg levels in the surface 15-cm layer was lightly calcined MgO (e.g., treatment G_0MgO). In this treatment, 36% of the amount originally added as MgO was extractable 6 yr later while in the treatment receiving calcitic dolomite (treatment G_0L), only 18% of the amount added was extractable (Table 3). Similarly, in the presence of 16 000 kg ha⁻¹ gypsum (treatment $G_{16}MgO$), the MgO source treatment maintained 20% of added Mg in extractable form while the treatment receiving calcitic dolomite ($G_{16}L$) showed only 12% in extractable form.

Manganese

In the unamended control, the level of Mn was greater at the surface and decreased with depth, similar to the distribution of Ca and Mg (Fig. 1). In this regard, the behavior of Mn contrasted with that of Al (another toxic cation associated with acidic soil) for which the concentration was greater deeper in the profile. Treatment F₁₅MgO reduced exchangeable Mn in the surface 2.5 cm to almost zero, and it and other treatments also reduced Mn at deeper depths (Fig. 7). The reductions in concentration can be attributed to treatment effects on pH, which is one of the factors controlling exchangeable Mn concentration (Ritchie, 1989). The amounts of exchangeable Mn found in any of the four layers of the treatments were correlated with mean organic C concentration and individual-layer pH [Mn (cmol_c kg^{-1}) = 1.11 + 0.0055 C (g kg^{-1}) - 0.24 pH, R^2 = 0.84, P = 0.001, n = 48].

Sulfur

Residual gypsum-induced increases in extractable S in the surface 15 cm were low (Table 3), supporting the observation that most of the gypsum had leached. The treatment with the greatest level of extractable S in the total 15 cm was treatment $G_{32}L$, and it had only 64 kg ha⁻¹ more S than the control. This is small in relation

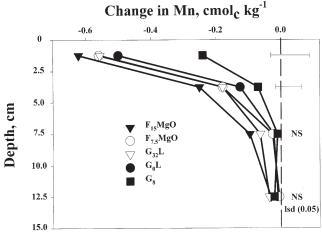


Fig. 7. Change in Mn at various depths for selected treatments sampled 6 yr after surface application of amendments to a Typic Hapludults abandoned pasture in southern West Virginia. (Treatments are described in Fig. 2.) Changes were calculated by comparing measured values with those found in the unamended treatment that received only fertilizer (G_0).

to the 6912 kg ha⁻¹ of S applied and small in relation to levels of extractable S as high as 2200 kg ha⁻¹ observed during the first 2 yr after application (Ritchey and Snuffer, 2002). Regression between added S and extractable S for all treatments showed that, on the average, less than 1% of the S added 6 yr earlier was still present in extractable form in the surface 15 cm [S extracted $(kg ha^{-1}) = 74 + 0.00904 S added (kg ha^{-1}), r^2 = 0.75,$ P = 0.0003, n = 12].

Plant Growth

Botanical Composition

In 1998, clover percentages averaged 6% in the subtreatments sown to clover (Table 4). Percentages of red clover or white clover, sown in the respective subtreatments, increased with TCE of the applied amendments. In the unseeded subtreatment, orchardgrass represented about 51% and tall fescue about 19% of the sward. Percentage orchardgrass was not related to treatment TCE, but percentage tall fescue increased significantly with amendment TCE (Table 4).

In 1999, the percentages of clover in the subtreatments sown to clovers increased to an average of 31% (Table 4). Clover percentage in these subtreatments was correlated with TCE of applied amendments, as was tall fescue percentage in the unseeded subtreatment.

Herbage Production

The 1665 kg ha⁻¹ overall mean herbage accumulation the year clover was sod-seeded (1998) (Table 4) was only 21% of the mean annual yield of 7800 kg ha⁻¹ harvested during the previous 2 yr (Ritchey and Snuffer, 2002). This was probably because no N fertilizer was applied (to stimulate clover establishment) while nitrogen fixation by the young clover plants was not sufficient to supply sward N needs. Moreover, precipitation during the last half of 1998 was 69% of the 30-yr average. There was no significant effect of clover sod seeding on herbage yield in the year of seeding, probably due to the small size of the clover plants. There was no significant relationship between 1998 herbage yield and TCE of applied amendments although there was a response for the previous 2 yr (Ritchey and Snuffer, 2002). The lack of TCE effect was presumably because N deficiency and low rainfall precluded expression of herbage yield differences.

In the first and second half of 1999, precipitation was 67 and 82% of the 30-yr average, but in spite of the continued low rainfall, mean herbage yields where clover was overseeded were 20% higher than those in the unseeded subtreatment where production was 1350 kg ha⁻¹ (Table 4). This indicated that in the absence of N fertilization, clover improved pasture productivity. Mean total herbage yield of the clover subtreatments for 1999 (Table 2) was correlated with clover content as estimated by botanical assessment [yield (kg ha^{-1}) = 1074 + 18.9 clover content (%), $r^2 = 0.73$, P = 0.0003, n = 12], and because clover content was correlated with amendment TCE, herbage yields in the clover subtreatments were also correlated with TCE (Table 4). The

Table 4. Botanical composition and herbage mass found in subtreatments sown to clover, or left unseeded, 6 yr after surface application of amendments with varying calcium carbonate equivalencies (TCE) at Bragg, WV. The range of values predicted by linear or quadratic regression for TCE = 0 to TCE = 9548 kg ha⁻¹ is given.

	1998			1999		
	Relationship	Mean	Predicted range	Relationship	Mean	Predicted range
Dorcontago in cucard				— ⁷ / ₀		
White clover in white	$\% = 0.8 + 0.0031TCE - 0.00000023TCE^2$; $B_2 - 0.04888 1.1$	7.8	0.8 to 9.7	$\% = 6.9 + 0.016$ TCE -0.000001 2TCE?; $B_2 - 0.03888 13$	45	6.9 to 50.8
Red clover in red clover	N = 0.04 - 0.05 N = 2.7 + 0.000524TCE; N = 0.37 + 0.000524TCE;	4.8	2.7 to 7.7	$N=0.02^{-1.5}$ % = 11.5 + 0.00227TCE; $r^2=0.46^*$; $n=12$	20	11.5 to 33.2
Subtreatment Tall fescue in unseeded subtreatment	r = 0.37; $n = 1.29/n = 7.66 + 0.0029TCE; r^2 = 0.80***n = 1.2$	19	7.7 to 35.5	% = 3.26+ 0.0035TCE; $r^2 = 0.69***; n = 12$	17	3.3 to 36.8
Orchardgrass in unseeded subtreatment	NS⊹	25	SN	SS	99	S
Herbage yield Red clover subtreatment	SX	1633a‡	NS kg	- kg ha ⁻¹ $Y = 1055 + 0.214$ TCE $- 0.000013$ TCE ² ;	1596a	1055 to 1914
White clover subtreatment	SN	1666a	NS	$K^2 = 0.91***; n = 12$ $Y = 1136 + 0.221TCE - 0.000015TCE^2;$	1661a	1136 to 1878
Unseeded subtreatment	SN	1695a	SN	$K^2 = 0.85$ cm; $n = 12$ NS	1350b	SZ

Significant at the 0.05 probability level.
* Significant at the 0.01 probability level.
*** Significant at the 0.001 probability level.
NS, not significant.

Values within the same year followed by the same letter are not significantly different at P=0.05.

Table 5. Coefficients of determination (R^2) for the relationship between clover-grass herbage yields in 1999 and individual plot soil characteristics estimated for various sampling depths using a quadratic model (yield = $a + bx + cx^2$) (n = 46).

Depth (cm)	Al	Ca	Mg	Mn	pН	Ca sat	Al sat
0 to 2.5	0.45***	0.44***	0.25***	0.34***	0.48***	0.44***	0.46***
0 to 5.0	0.39***	0.41***	0.24**	0.29***	0.48***	0.42***	0.40***
0 to 10	0.30***	0.35***	0.26**	0.21**	0.47***	0.36***	0.34***
0 to 15	0.25**	0.31***	0.29***	0.09	0.48***	0.32***	0.32***

^{**} Significant at the 0.01 probability level.

correlation of herbage yield with clover percentage and the correlation of percentage clover with amendment TCE support the hypothesis that increased yields observed in the plots seeded to clover were associated with increased prevalence of clover plants made possible by amendment action in reducing soil acidity. Clover probably increased yield because it fixed atmospheric N. In the unseeded grass-only subtreatment, herbage yields did not vary with amendment TCE. Apparently, unfertilized orchardgrass and tall fescue were so limited by N deficiency that responses to soil acidity factors were not expressed.

Predicting Yields Using Several Potential Sampling Depths

We estimated potential soil chemical characteristics for the top 5-, 10-, and 15-cm layers by calculating weighted means from values measured in individual shallower layers. Mean values for nutrients decreased as potential sampling depth increased, as would be expected from examination of the nutrient distributions (Fig. 2, 3, and 5). Similar results were obtained by Bryan and Elliott (1991), who studied the effect of depth of sampling in an Aquic and Ultic Hapludults pasture in northern West Virginia that was surface-fertilized. They found that increasing sampling depth from 0 to 2.5 cm to 0 to 7.5 cm decreased mean levels of pH, P, Mg, and K where fertilizer and limestone were applied 3 yr previously. They called attention to the importance of sampling depth in evaluating pasture fertility status. In pastures where soil is periodically cultivated, one would

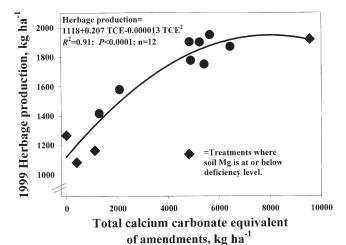


Fig. 8. Mean 1999 grass-clover herbage production in subtreatments sown to clover as related to total calcium carbonate equivalent (TCE) of amendments surface-applied in 1993. Treatments with levels of exchangeable Mg (0 to 2.5 cm) lower than the West Virginia University-established sufficiency level are indicated.

expect that varying the depth of sampling would have little effect on soil analysis because of the mixing that occurs each time the field is tilled. However, where nutrients and amendments were not mechanically incorporated, depth of sampling will make a big difference in measured chemical characteristics. West Virginia University recommends a sampling depth of 0 to 5 cm for permanent pastures and 0 to 15 cm for tilled cropland and a split sampling of 0 to 2.5 cm plus 2.5 to 15 cm for no-till corn (van Eck and Collier, Jr., 1995).

We examined the quadratic relationship between clover-grass herbage and individual plot soil parameters for four potential sampling depths (0 to 2.5, 0 to 5, 0 to 10, and 0 to 15 cm) (Table 5). Coefficients of determination for the regression between 1999 herbage yield and soil characteristics on an individual-plot basis showed that the best values were generally for soil parameters measured in the 0- to 2.5-cm layer (Table 5). This indicated that under the conditions of our experiment where an infertile field was being renovated by surface application of amendments and fertilizers, the most important soil layer was the layer where the most benefit of amendments (and probably P fertilizers) was present, namely the top 2.5-cm layer. However, these results cannot be used to interpret the influence of deeper soil layers had they been of high pH and fertility status because we did not test this.

On a per-treatment basis, the quadratic relationship between mean treatment herbage yield and mean soil-acidity-related parameters pH, Mn, Al, Ca, and Al saturation measured in the 0- to 2.5-cm layer explained 81 to 92% of the variability in measured yields. This indicated that much of the improvement in productivity in clover subtreatments in this experiment could be attributed to the effect of amendments in overcoming acidity limitations. Potassium levels (0.26 to 0.55 cmol_c kg⁻¹) were in the high to excessive range as defined by West Virginia University and decreased as yield increased, perhaps reflecting increased uptake into plant tissue (data not shown). Soil P levels were not measured but were probably adequate as the amount of P applied totaled 468 kg ha⁻¹ over the 6 yr of the experiment.

The relationship of 1999 herbage production to TCE was well described by a quadratic equation: production $(kg ha^{-1}) = 1118 + 0.2072 TCE - 0.000013 TCE^2; R^2 = 0.91***, <math>n = 12$ (Fig. 8). An alternative relationship taking into account a possible Mg deficiency effect in the four treatments where soil Mg (0 to 2.5 cm) was less than the "sufficient" levels established by West Virginia University is: production $(kg ha^{-1}) = 1044 + 0.0871 TCE + 284.3 Mg$ (0 to 2.5 cm); $R^2 = 0.93***, n = 12$. The lower yields observed at the two ends of the

^{***} Significant at the 0.001 probability level.

regression curve can be explained by (i) Mg deficiency or (ii) a curvilinear response to liming effects. The quadratic response illustrated in Fig. 8 is probably the more accurate explanation because including soil Mg did not significantly improve quadratic regressions between production and TCE, soil pH, Ca, or Al (data not shown). The herbage yield increase calculated from the regression equation in Fig. 8 attributable to application 6 yr previous of 4654 kg ha⁻¹ calcitic dolomite with a TCE of 4840 kg ha⁻¹ was 698 kg ha⁻¹. At a value of \$70 per 1000 kg for grass—clover hay, the value of the increase in yield was \$49 ha⁻¹.

In summary, we found that in an unamended grassland, Ca and Mg concentrations were higher in the surface 2.5 cm than in lower layers. Where amendments were surface-applied 6 yr earlier, enrichment of the surface 2.5-cm layer was even greater. Calcitic dolomite, FBC, and MgO reduced soil acidity, but 6 yr after application, gypsum had little effect on chemical properties except for a reduction in Mg. Decreased soil acidity associated with calcitic dolomite, FBC, and MgO increased clover occurrence and grass-clover herbage production. The residual effect from even heavy gypsum applications did not improve production (except for a small benefit from 5% TCE associated with a CaCO₃ component) and, for treatments where adequate Mg supplements were not included, caused soil Mg levels to decrease. Where amendments were surface-applied to an abandoned pasture, soil Al saturation, Ca saturation, Al, Ca, and Mn in the top 2.5-cm layer tended to show stronger correlations with yields than soil properties from deeper soil layers. We conclude that surfaceapplied liming amendments containing Ca and adequate Mg can influence botanical composition of a sward and increase herbage productivity, offering dual benefits in terms of by-product use and renovation of acidic soils.

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